THE INFRARED ABSORPTION SPECTRUM OF WATER VAPOR BEYOND 10μ

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

Ann Arbor

BY

LOUIS RUSSELL WEBER

1932

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

BY

LOUIS RUSSELL WEBER

1932

*1637

R. UNIV.
BIBLIOTHEEK
LEIDEN

The Absorption Spectrum of Water Vapor Beyond 10μ

By Louis Russell Weber
Physical Laboratory, University of Michigan.

(Received March 9, 1932)

The absorption spectrum of water vapor has been remeasured in the region 10–25μ, the dispersing agent being a 60° KBr prism with a Wadsworth-Littrow mounting. The recording vacuum spectrograph is described. The necessary amplification is obtained by means of the Moll or the Firestone amplifier. The increased dispersion of this spectrograph shows the spectrum to be very complicated in this region and not yet fully resolved. No decision has been reached as to the nature of this spectrum, whether it is a vibration-rotation band, the near end of the rotation spectrum, or an overlapping of the two.

THE new vacuum recording spectrometer,[1] recently described, possesses a range which extends to about 30μ. This increased spectral range in a region of the spectrum until now little explored, is due to the complement of prisms, made from single crystals grown in this laboratory from the fused salts. The materials so far successfully fashioned into prisms are potassium chloride, potassium bromide and potassium iodide. This instrument holds promise of usefulness, particularly in the region beyond 15μ, the limit set by the opacity of sodium chloride. The prism spectrometer possesses the obvious advantage in distinction to a grating of conserving the energy available in a single spectrum. By using one or more prisms in a train and reversing the beam, a dispersion approximating that of a grating may be obtained. The crystals besides making prisms, also furnish materials for windows of absorption cells, for vacuum thermopiles, etc.

The first extensive work with this instrument has been with water vapor. Its spectrum has been extensively studied in this laboratory[2] up to and through the band at 6μ which extends well beyond this central point. There appeared to be the possibility of deciding through the largely increased resolution of this instrument whether the bands known to exist beyond 10μ were pure rotation bands or were another vibration-rotation band. Moreover, it is necessary to know the water vapor spectrum as produced by this spectrometer whenever the instrument is used with other materials, provided any part of the beam from source to recording thermopile passes through the air of the room. This is because the water vapor of the air is always present in sufficient quantities to produce marked absorption lines, particularly beyond 15μ. To a lesser extent the carbon dioxide of the air presents a similar problem.

The self-recording spectrometer used in this work has some marked advantages. With the present instrument, it is possible to record a spectral

[1] Randall and Strong, Rev. Sci. Inst. **2,** 585 (1931).

[2] Sleator, Astrophys. Journ. **48,** 126 (1918); Sleator and Phelps, Astrophys. Journ. **62** 28 (1925); Sleator and Plyler, Phys. Rev. **37,** 1493 (1931).

range of 15μ in one and one-half hours. One can keep the conditions of the source, absorption cell, and spectrograph more constant than is possible when several days are required for one complete set of measurements. Furthermore, a recording spectrograph makes a continuous record, leaving nothing to the conjecture of the experimenter as to what takes place between circle readings taken at definite intervals. The saving in time thus gained can be used for making several records. This not only makes precise measurements possible but permits the elimination of extraneous influences with greater certainty.

The spectrometer Fig. 1 is a Wadsworth-Littrow combination, using a 60° prism of potassium bromide. The radiation enters the slit S and is reflected by the small mirror M''' to the parabolical mirror M, 14 cm in diameter. This mirror, M, is a segment cut from a larger paraboloidal mirror in such a manner that the axis of the paraboloid passes through the edge of the mirror, M. M is so adjusted that this axis passes midway between the slit S' and the virtual image of S. Since these are close together the aberration is reduced to a minimum. In order that the more essential features of the instrument may be seen readily, the supports which carry the slits S and S' are not shown in

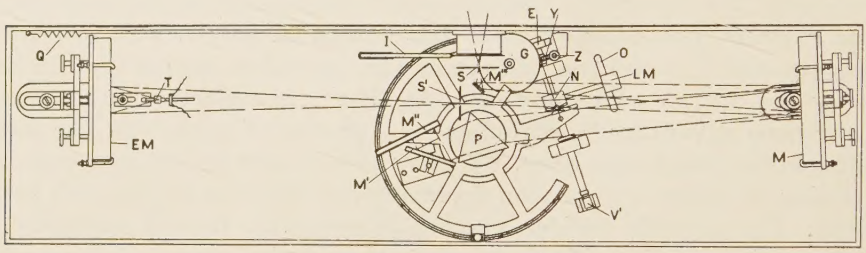

Fig. 1. Inner brass compartment of the spectrograph containing optical parts.

the figure. The rays after being made parallel by M, pass through the prism P at almost minimum deviation. The Wadsworth mirror M' which moves with the prism, reflects the rays to the Littrow mirror M'' which is stationary so that they strike the latter almost normally. Retracing their path, they again pass through the prism at nearly minimum deviation to the mirror M which brings them to focus on the exit slit S'. This slit of 25 mm length, is at one of the foci of the elliptical mirror EM, and the thermopile T is at the other focus. These foci are 43.75 and 8.75 cm from the mirror, so as to produce an image on the thermopile junctions one-fifth the size of the exit slit. The spectrograph as described is enclosed in a heavy brass case, which in turn can be rolled into a heavy welded steel case. This latter case is so designed that any deformations produced by evacuation can in no way affect the brass case. The complete spectrograph is evacuated to pressures varying from 10^{-3} to 10^{-4} mm using a fore pump working with two mercury diffusion pumps.

The thermopile and its mounting were designed by Firestone.[3] The three junctions are composed of bismuth and an alloy of bismuth and tin. Since the

[3] Firestone, Rev. Sci. Inst. **1**, 630 (1930).

linear thermopile was enclosed in a case only 10 mm long, it intercepted very little energy when placed in front of the elliptical mirror. The sensitivity increased approximately nine-fold when the case was evacuated to 10^{-3} mm.

The potassium bromide prism was made from a single crystal which was grown in the laboratory from the fused salt, and has a refracting angle of approximately 60°. The faces are 6.5 cm high and 7 cm long. The theoretical resolving power, computed from the indices of refraction recently measured by Gundelach,[4] is 366.8 at 10μ and 1295 at 25μ.

The practical resolving power in which we are primarily interested because of our finite slit widths is shown in Table I in which the slit-widths are

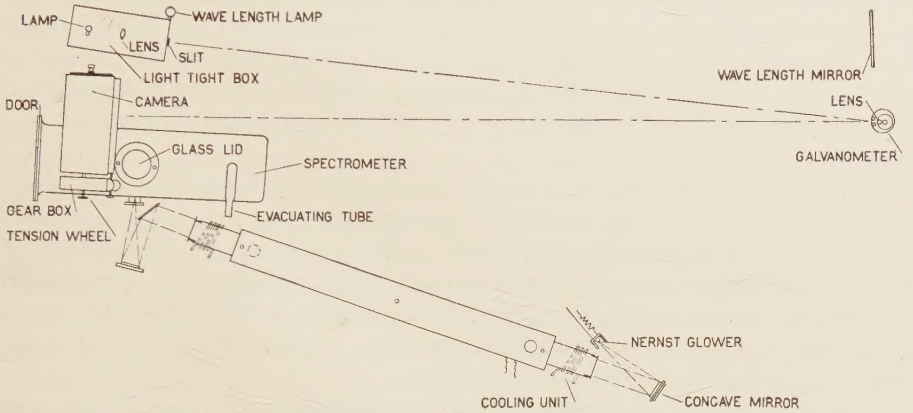

Fig. 2. Arrangement of apparatus showing the outer welded steel case containing the spectrometer, the camera, the absorption cell, and the registering equipment.

TABLE I. *Practical resolving power of spectrometer.*

Slit width	Region	Wave number	Angstroms	Seconds	Hettner
	10μ	5.90	590		700A
0.2 mm	17	1.18	340	20.7	3900
	23	0.43	240		17400
	10	11.80	1180		
0.4 mm	17	2.36	680	41.4	
	23	0.86	480		

given in terms of wave number, angstrom units, and seconds of arc. For comparison Hettner's slit widths are included. Thus, at 23μ, the interval included by the slit is 70 to 35 times smaller than that used by Hettner,[5] depending upon the slit used. At 17μ, the interval is 6 to 12 times smaller. The present determinations were made with these two slit widths 0.2 mm from 10 to 15μ and 0.4 mm from 15 to 25μ. The exit slit was kept at the same value as the entrance slit.

Two lengths of absorption cell were used, of two meters and three meters respectively. Fig. 2 shows one of the cells in detail. It was composed of several

[4] E. Gundelach, Zeits. f. Physik **66,** 775 (1930).

[5] Hettner, Ann. d. Physik **55,** 476 (1917).

lengths of galvanized iron pipe 6″ in diameter joined together rigidly by partly telescoping one section into the other. In each end a brass ring was fitted snugly and sealed with liquid porcelain. These rings had been prepared so that a shoulder extended beyond the end of the cell for the purpose of receiving the holders of the lacquer films used to close the ends. This permitted an airtight joint.

Besides the ends, the cell had three 1″ openings to receive thermometers, one at each end and one in the middle. The gas inlet and outlet were placed, one on top at one end, and one on the bottom at the other end to insure a more uniform filling of the cell. They were 3″ in diameter. The whole cell, except for 15 inches at each end, was covered with a layer of asbestos paper which was wound with resistance wire to permit heating the cell to 350°C if necessary. In order to reduce temperature changes in the room as much as possible and to keep the cell at a more uniform temperature, a cylinder of magnesium and asbestos was fitted around the cell. The whole was further covered with canvas.

Since the lacquer films were easily ruptured at high temperatures, it was necessary to cool the ends of the cell by running water through six or seven turns of lead tubing wound around each end. To make films whose diameters were five inches, we placed three small wires equispaced along diameters of the ring and in the plane of the ring. These intercept very little energy and make the film much more capable of standing up under its own weight or any vibrations to which it might be subjected.

The films were approximately 0.5μ in thickness and transmitted practically all the radiation in the region from 10μ to 25μ except at 12μ where the absorption amounted to about 80 percent. They were removed when this region was under investigation. In working with steam in the region from 10μ to 25μ, it is not absolutely necessary to have the ends of the cell closed, provided any mirrors near the cell are protected from condensation or are sufficiently removed so that no condensation takes place on them.

The source consisted of a small Nernst glower enclosed except for one side, in a small asbestos box. Although the glower was operated on the alternating current lighting circuit, no trouble was experienced in fluctuations. It was placed very near to the end of the cell as shown in Fig. 2 and at the principal focus of a concave silvered mirror whose diameter was 12 cm and whose focal length was 25 cm. Thus, the rays traversing the cell were parallel, and upon emerging from the cell, fell upon a plane silvered mirror 20 cm in diameter. This mirror was far enough from the end of the cell so that when no films were used, no condensation took place on it. The rays were then reflected to a gold plated concave mirror and brought to focus on the entrance slit of the spectrometer which was covered by a potassium bromide plate to make possible the evacuation of the spectrograph.

The main features of the recording system were as follows. The thermopile was connected to a Moll thermal relay for most of the work; later, to eliminate all drifts, an alternating current amplifier due to Firestone was used. This will be described in more detail below. The amplification used with the

Moll relay was approximately 45 which gave deflections of 50 cm at 10μ to 3 cm at 25μ for slits of 0.2 mm width. The distance from the galvanometer to the camera is 4.5 meters. The amplification was limited by the Brownian motions affecting the galvanometer coil and also by the drifts that might be present. By means of the lamp and optical system shown in Fig. 2, a point image of the slit in the end of the light-tight box was produced on the photographic paper in the camera. The drum holding the photographic paper moves perpendicular to the deflection of the galvanometer and in coordination with the prism.

The whole mechanism for causing the coördinated movement of drum and prism was driven by a small universal motor. A Veeder counter placed on the spectrograph allowed one to read the position of the prism in arbitrary numbers which were approximately equal to seconds of arc. Since the calibration to be described shortly, consisted in getting the wave-lengths as a function of these Veeder numbers, the Veeder counter was always used to set the prism for throwing radiation of a certain wave-length into the exit slit. For every 30 seconds of arc turned through by the prism, a contact was closed on the spectrograph case, causing the lamp labelled "wave-length lamp" to flash. The light from this lamp was reflected back by a plane mirror near the galvanometer and entered the camera producing a fine reference line on the photographic paper with the aid of a cylindrical lens whose length equals that of the camera box. Thus, as we shall see later, this makes the measurement in terms of wave-length quicker and limits the error due to a shrinkage of the paper to a negligible amount. The bromide paper sheets were 20×31 inches so that the region from 10 to 23.5μ could be recorded on one sheet during one revolution of the drum in 90 minutes of time. The drum was usually operated so that the time between reference lines on the paper was 15 seconds and the distance between them was 2.5 mm. Several records were taken with a time interval of 114 seconds and a distance between lines of approximately 8 mm. This interval still represented 30 seconds of arc with respect to the prism.

When the present investigation was near an end, Mr. Firestone had just perfected an amplifier which eliminated all drift of the zero. A full description of this has just appeared[6] so only a brief account will be included here. In merely by connecting a large condenser in series with the galvanometer (across which is a shunt resistance for critical damping), and then periodically interrupting the radiation falling on the thermopile. The galvanometer would then give an oscillating deflection, the amplitude of oscillation being proportional to the amount of radiation falling on the thermopile. But since the drifts can not pass through the condenser, the oscillations of the galvanometer will always take place about the same zero. However, any condenser to be found in the laboratory would have such a high impedance at these low frequencies that the sensitivity of the system would be too low. By using a photoelectric cell and vacuum tube in the system to amplify the deflections of the primary galvanometer, circuits of sufficiently high impedance are en-

[6] Firestone, Rev. Sci. Inst. **3**, 163 (1932).

countered that condensers may be connected in series with them without seriously imparing the sensitivity. Thus, although the primary galvanometer may be subject to a considerable amount of drift, the secondary galvanometer, which is making the record, receives only the periodic deflection, the drift not being passed through the amplifier. All galvanometer, amplifier, and thermopile leads were enclosed in copper sheathing to eliminate electrical disturbances either from circuits in the room or other apparatus in the building.

Although the spectrograph was equipped with a very good circle to be read by means of a sealed-in microscope, it was believed that a much quicker method of calibration would be an empirical one. Therefore, the absorption spectra of gases previously measured with a grating to 15μ were recorded and a curve was then plotted between the known wave-lengths and their Veeder numbers as read on the instrument.

TABLE II. *Substances used and their absorption wave-lengths.*

Substance	(Wave-length) μ in air	Veeder number	Wave-length	Veeder number
Ammonia[7]				
	10.32μ	42400	20.29**	47975
	10.71	42550	20.42	48062
Acetylene[8]	13.69	43810	20.62	48230
Methyl Iodide[9]	11.29	42765	20.82	48394
Methyl Iodide[9]	11.90	43000	21.12	48619
Methyl Bromide[10]	16.38	45260	21.34	48784
Carbon Dioxide[11]	14.97	44475	21.82	49203
Water Vapor*	15.991	45052	22.07	49401
	16.190	45181	22.88	50135
	16.667	45452	23.81	51004
	16.893	45593	24.61	52069
	17.102	45723		
	17.220	45799		
	17.360	45884		
	19.023	46999		

Data beyond 15μ has been kindly supplied by Mr. Norman Wright and Dr. E. K. Plyler, who were working with gratings in the region beyond 15μ. Mr. Wright had found water vapor absorption superimposed upon the energy curve of reststrahlen from quartz in the region of 20μ. The pattern was so unmistakably the same as obtained previously on the recording spectrograph when 0.8 mm slits were used that these series of points were used for extending the calibration curve. They were measured with a grating with an accuracy of 0.01μ. In taking "in and out" readings in the absorption spectrum of another gas in the near infrared, Dr. E. K. Plyler noticed that the "out" readings varied considerably due to atmospheric absorption. He very kindly

[7] Barker, Phys. Rev. **33,** 684 (1929).
[8] Meyer and Levin, Jour. Op. Soc. **16,** 137 (1928).
[9] Bennett and Meyer, Phys. Rev. **32,** 888 (1928).
[10] Sleator, Phys. Rev. **38,** 147 (1931).
[11] Martin and Barker, Phys. Rev. **37,** 1708 (1931).
* Checked from "out" curves of Plyler.
** Duplicated by Wright.

permitted the writers to plot these values and a number of these bands were found to correspond with those already found in our work. Dr. Plyler's readings are accurate to $\pm 0.001\mu$. It is believed the points can be taken from the dispersion curve with an accuracy of $\pm 0.01\mu$. An inspection of the entire calibration curve from 1 to 25μ shows that it follows the general characteristics of dispersion curves for other salt prisms.

The substances used and their wave-lengths of absorption are given in Table II.

Since this recording spectrograph is just coming into general use, its method of recording data will be described with some detail. The spectrograph was generally evacuated to 10^{-4} mm of mercury pressure before a record was made. If the region from 10μ to 15μ was under investigation, steam was led from the generator into the top of the cell at one end, the cell being heated to over 100°C. If, on the other hand, the region from 15μ to 25μ was to be recorded, a long trough containing water was placed in the bottom of the cell. This produced saturated water vapor at room temperature. After all conditions regarding amplifier, cell, and spectrograph were believed constant as learned by experience, the camera was loaded and the register lamp adjusted. The shutter in front of the camera was opened, exposing the cylindrical lens and the photographic paper. Finally, the metal shutter in front of the entrance slit was raised. The small driving motor was then started after the Veeder number had been recorded. For convenience, the instrument was always started when the circuit of the lamp used to record the reference lines was closed. By pausing a second after the camera shutter was opened, a darker reference line was produced on the paper than those made in the course of the record. Hence, there was no doubt about the initial Veeder number.

At intervals of about 1000 Veeder numbers, the motor was stopped and the metal shutter in front of the entrance slit was closed. This recorded the deflection photographically on the paper. Afterwards, a line drawn through these points furnished a base line with the aid of which percentage absorptions could be estimated. With the Firestone amplifier described above, the zero point of course always remained the same.

Sometimes, more than one record was obtained on the same sheet thus making a rapid comparison of curves possible. In this case, the reference lines were not put on a second time, experience having shown that the second set of reference lines either exactly coincided with the first set or were displaced at most by an amount corresponding to not more than one or two seconds of arc. The exact amount of this displacement could be determined by recording only a few of the subsequent sets of reference lines, and allowed for in reading the positions of the corresponding set of absorption lines.

Only those absorption lines that appeared on four or five records were accepted. The most intense lines always appeared; but the weakest ones could be influenced by the Brownian motion affecting the galvanometer so that care had to be exercised in making these determinations.

The greatest difficulty presents itself in the determination of percentage absorption. The energy is small at best and the percentage of spurious radia-

tion of shorter wave-lengths increases as 25μ is approached. If one can move the absorption cell in and out of the path, one can, by compensating devices, obtain the percentage absorption with a fair degree of precision. In the present case, the cell is too massive to lift out of the path and, furthermore, such a method is impossible with continuous recording. Also since carbon dioxide and the water vapor which is under investigation are always present in the atmosphere, the optical path cannot be entirely freed of them.

The method of determining the percentage absorption was as follows: (1) With the Moll relay. When employing this device, deflections were taken several times on a record by stopping the driving motor and closing the metal shutter in front of the entrance slit. A small dot was made on the paper in this way and the line of zero deflection of the galvanometer was found by drawing a smooth curve through these points. An envelope of the absorption curve was then drawn to determine the position the curve would have had

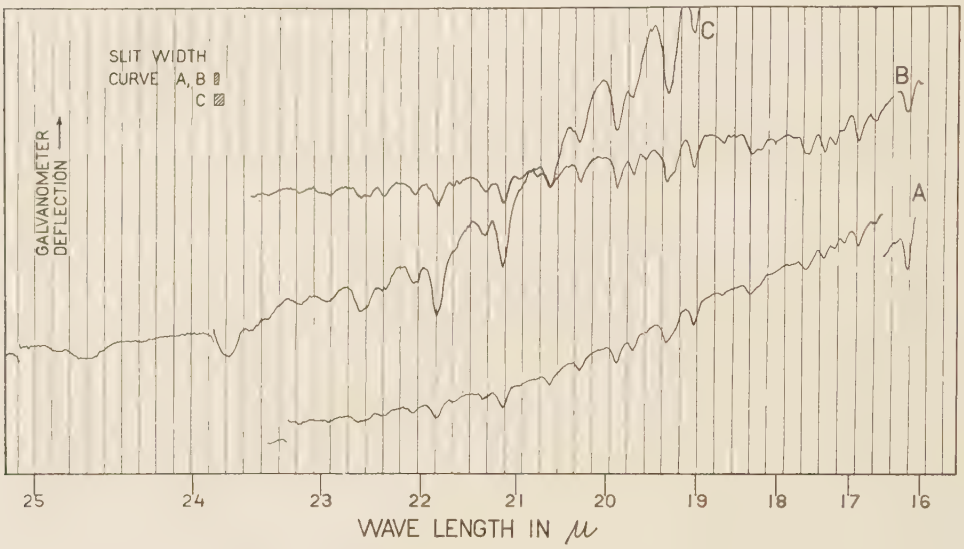

Fig. 3. Absorption lines in the region between 16μ and 25μ photographically registered, the amplification being by the Moll amplifier. Cell filled with saturated vapor at room temperature. Slit width curves *A* and *B*, 0.4 mm, *C*, 0.8 mm.

provided there were no absorption. The depth of the absorption was measured with respect to this envelope and the ratio of this distance to the distance between the envelope and the base line gave the percentage of absorption. Since there is always some scattered radiation of shorter wave-lengths, several deflections were taken in the region from 10μ to 20μ with a fluorite plate placed in the optical path before the entrance slit. Likewise a rocksalt plate was used in the region from 20μ to 25μ. Corrections were then applied to the apparent absorptions taking account, of course, of the loss of radiation due to the reflections from these plates and also a possibility of a slight change in focus. We believe that the percentage absorptions given later in the table will at least give the relative intensities with fair degree of accuracy. (2)

With the Firestone amplifier. Here the zero remains constant so that one can draw an envelope at the top and at the bottom of the recorded oscillations of the galvanometer. The available energy is then for any wave-length, one-half the distance between the envelopes while the transmitted energy is one-half the width of the record at the same wave-length. To get the percentage absorption, one merely subtracts the second value from the first one and divides this result by the first value. A correction for the scattered radiation must be made as before.

Figs. 3 and 4 show the curves obtained in the region from 10μ to 25μ as recorded with the Moll relay and the recording spectrograph. Of the three curves of Fig. 3, recording the region beyond 16μ, A and B were obtained when a slit width of 0.4 mm was used, while a slit width of 0.8 mm was used when C was recorded. The absorbing medium was saturated water vapor at room temperature obtained by placing a trough of water in the bottom of the

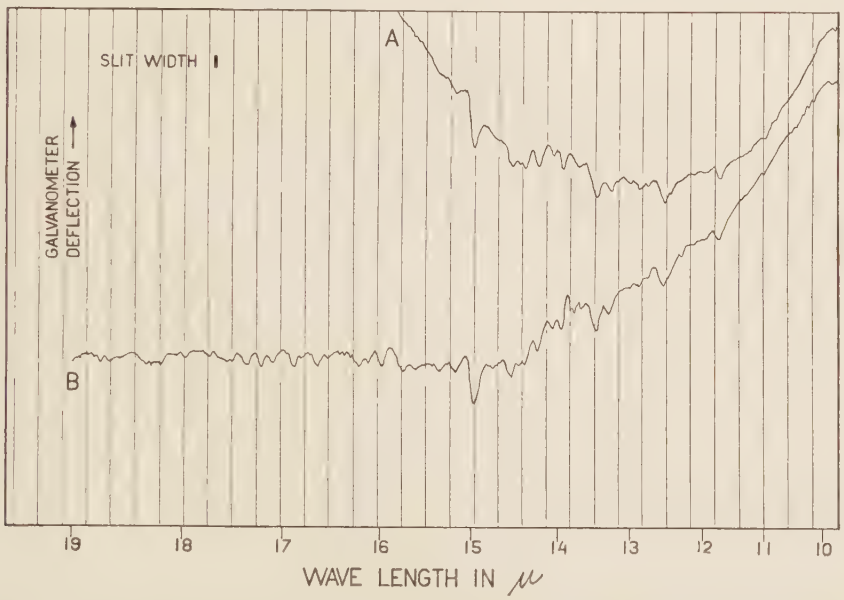

Fig. 4. Absorption lines in the region between 10μ and 19μ. Cell filled with steam for curves A and B. Slits 0.2 mm, Moll amplifier.

cell. The cell was not heated. B and C were recorded on the same sheet but A has been cut from another record and fitted for comparison. It is apparent that all of the lines repeat themselves very accurately. Curve C, however, which was obtained with twice the slit width of the other does not show as many lines resolved. In the reproductions of the original records only every fifth reference line has been drawn in.

The spectral region from 10μ to 19μ is recorded in Fig. 4. The curves shown were taken with slit widths of 0.2 mm since the available energy in this region was greater. With steam filling the three meter cell, and the cell heated to over 100°C, curves A and B were obtained. The fact that they do not have the slope of the other curves was due to a slight drift in the thermal relay

from the heat caused by the cell. Otherwise, they would have followed the energy curve of the glower except for the absorption present. If the drift is not too great, it is a distinct advantage, especially when one is in a region where the slope of the energy curve is great. As the curves clearly show, the falling off of energy is compensated by a drift so that the absorptions appear with less distortion than they otherwise would. As it was, the drift in a did become large enough to change the slope to one in the opposite direction.

Both Hettner's work and the present one, show the least absorption in the region from 10μ to 11μ. The strong line at nearly 15μ is due to CO_2 in the atmosphere. The region from 16μ to 19μ shows additional lines to those recorded in Fig. 3 since the resolution is larger here due to the narrower slit. It is unfortunate that lack of sufficient energy prevented a continuance of the curve out to 25μ with slits 0.2 mm wide. The ability of the instrument to repeat itself is shown by these curves and also those in the previous plates.

Several records, one of which is shown in Fig. 5, were obtained while using the Firestone amplifier already described. Due to the unvarying zero and the ease with which envelopes can be drawn to these curves, percentage absorptions can be obtained much more easily than with the Moll instrument. The results derived from them substantiate those of the previous work and add several new lines. Some of the records with the Firestone amplifier were made with the camera drum rotating three times as fast with respect to the prism as was the case when the curves of Fig. 5 were recorded. Then by running the driving motor so slowly that 114 seconds of time would elapse between reference lines instead of the usual 15, it was possible to obtain 30 instead of 4 complete oscillations of the galvanometer recorded between the reference lines, or one to each second of arc, since in terms of arc the reference lines are still but 30 seconds apart. Thus the spectrum was covered at much shorter intervals than is usually done when the circle is advanced by small steps without automatic recording.

Fig. 5 was obtained when the cell contained saturated water vapor at room temperature. The slit width was 0.5 mm. The increase in deflections at 16μ and again at 22μ is due to an increase of the amplification used. As in Fig. 4 very little absorption is evident in the region between 10μ and 15μ without having steam in the cell as the absorbing medium. That which is present is due mostly to CO_2.

Records in the region beyond 16μ, obtained when the slits were 0.2 mm with steam filling the cell, did not show sharper lines due undoubtedly to the fact that steam is too absorbing in this region. For this reason, only saturated water vapor at room temperature was used in this region to obtain the best records. Besides water vapor, the CO_2 content of the air also absorbed. Careful check experiments, in which the change in intensities of the lines were observed when the three meter cell was filled in turn with steam, CO_2, and dried air, determined which of the observed lines were due to water vapor and which to CO_2. Table III contains the results of this research.

The measurement of the water vapor spectrum as resolved by this recording spectrometer has been accomplished. But the question as to whether this

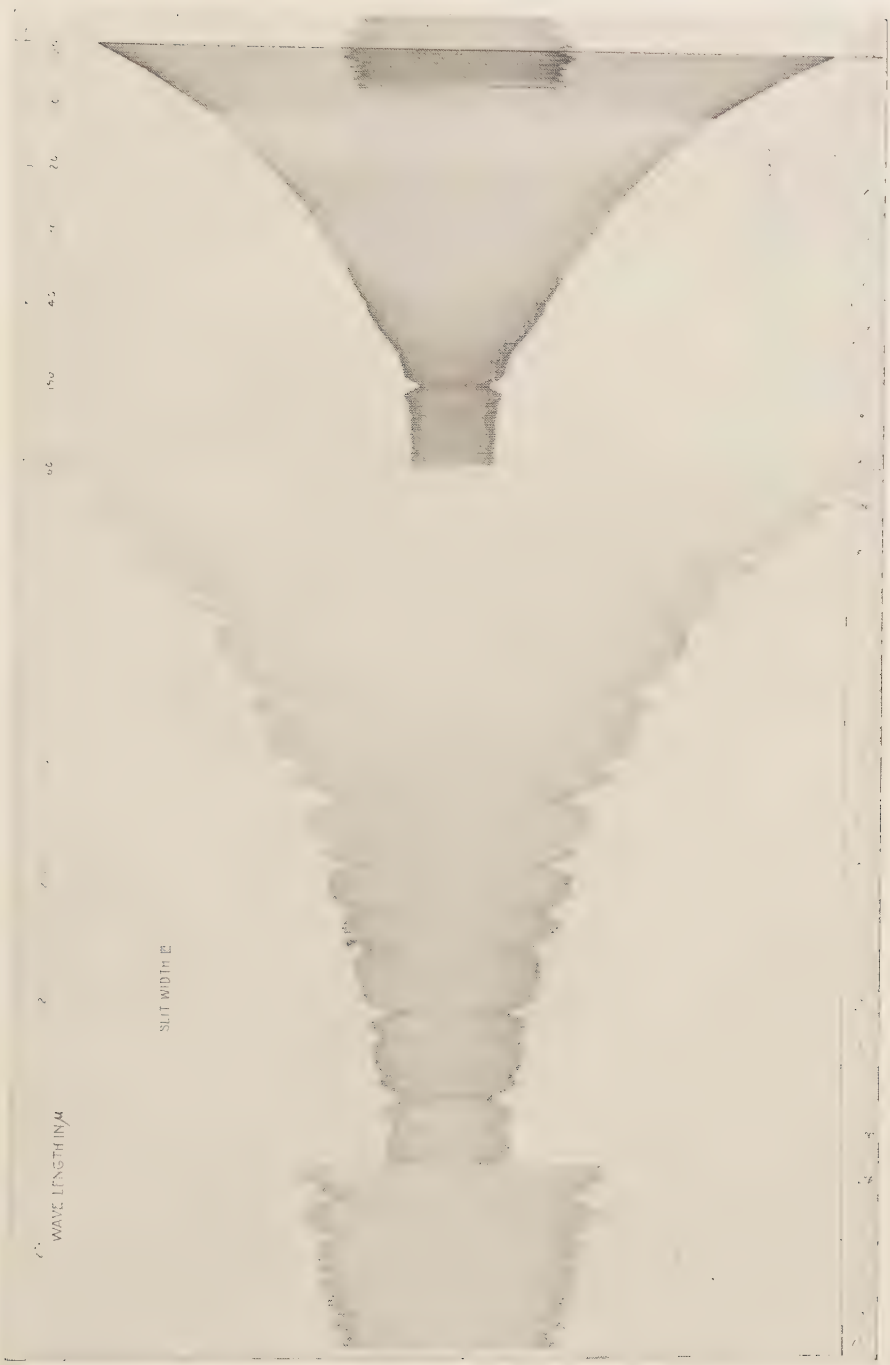

Fig. 5. Absorption lines in the region between 10μ and 23μ absorption cell filled with saturated water vapor at room temperature. Slits, 0.5 mm. Firestone amplifier used. Reference lines appear reproduced only at the extreme right of figure.

TABLE III. *Absorption spectrum of water vapor.*

Wave-length	Waves per cm	% Absorp. steam		Wave-length	Waves per cm	% Absorp. sat. vapor
10.13μ	987.2	1		16.58μ	603.1	2
10.20	980.4	1		16.667*	600.0	5
10.42	959.7	9		16.69	599.2	3
10.85	921.7	1		16.82	694.5	7
11.06	904.2	5		16.893*	592.0	14
11.22	891.3	1		17.102*	584.73	6
11.32	883.4	1		17.220*	580.72	13
11.55	865.8	1		17.360*	576.04	14
11 58	863.6	1		17.50	571.4	4
11.65	858.4	2		17.57	569.2	16
11.77	849.6	7		17.64	566.9	9
11.97	835.4	4		17.72	564.3	6
12.14	823.7	7		17.84	560.5	4
12.34	810.4	2		17.95	557.1	6
12.41	805.8	4		18.06	553.7	9
12.48	801.0	10		18.21	549.1	14
12.58	794.9	11		18.29	546.7	8
12.65	790.6	15		18.34	545.3	19
12.82	780.0	6		18.39	543.8	7
12.92	774.0	9		18.52	540.0	5
13.06	765.7	17		18.66	553.9	8
13.22	756.4	16		18.74	533.6	3
13.32	750.8	15		18.97	527.1	4
13.50	740.7	17		19.023*	525.68	21
13.74	727.8	9		19.10	523.6	5
13.95	716.8	18	CO_2	19.25	519.5	24
14.07	710.7	13		19.32	517.6	32
14.23	702.7	32		19.41	515.2	6
14.39	694.9	31		19.56	511.2	9
14.46	691.6	32		19.69	507.9	23
14.54	687.8	39		19.79	505.3	20
14.76	677.5	21		19.87	503.3	30
15.17	659.2	25		20.10	497.5	3
15.34	651.9	17		20.29*	492.9	24
15.40	649.4	23	CO_2	20.42*	489.7	4
15.55	643.1	23		20.53	487.1	7
15.62	640.2	24	% Absorp.	20.55	486.6	18
15.73	635.7	32	Sat. Vapor	20.62	485.0	28
15.92	628.1	22	1	20.76	481.7	9
15.991*	625.35	40	4	20.94	477.6	12
16.08	621.9	19	1	21.12*	473.5	53
16.11	620.7		6	21.14	473.0	43
16.190*	617.67	25	10 CO	21.18	472.1	23
16.38	610.5	9	2	21.29	469.7	22
16.53	605.0	14	1	21.34*	468.6	26
21.39	467.5	12		22.62	442.0	31
21.66	461.7	24		22.88*	437.0	21
21.74	460.0	39		22.98*	435.1	9
21.81	458.5	65		23.16*	431.8	10
21.85	457.7	42		23.44*	426.6	24
21.89	456.8	21		23.59*	423.9	42
22.07	453.1	35		23.81*	420.0	66
22.37	447.0	42		24.61*	406.3	28
22.39	446.6	42		24.72	404.5	38
22.55*	443.4	17		24.91	401.4	25

* Checked with grating.

system of lines belongs to the rotation spectrum or to the vibration-rotation spectrum, or an over lapping of the two, can not now be decided. Theory indicates that the pure rotation spectrum in this relatively short wave-length

region is very complicated. The interpretation of the rotation spectrum can probably best be approached from measurements at the long wave-length end of the spectrum. The experimental difficulties would then be greatly increased but the interpretation of the results would be correspondingly simplified. A plot giving the percentage of absorption as a function of the frequency shows an increasing absorption with increasing wave-length. Unfortunately circumstances have not permitted extending this investigation at this time beyond 25μ. If it could have proceeded to 30 or 35μ, it might have become definitely evident that the absorption was continuously increasing, or it might have shown a maximum. The first case would have indicated a rotation spectrum, the second a vibration-rotation band.

A slight appearance of symmetry, which is more evident in some of the other records than in those shown here, would indicate a vibration-rotation band with its center at 18.7μ approximately. On the other hand, such changes in intensity as occur in passing from saturated vapor at room temperature to steam at somewhat over 100°C are very irregular, a circumstance more in harmony with the supposition that the near end of the complicated rotation spectrum is involved than that a vibration-rotation band is concerned. It is possible that if a sufficiently high elevation of temperature of the absorbing vapor could be produced, such changes in the relative intensities of the observed lines would occur as would permit a decision as to which type of spectrum is involved, since the change in relative intensities would be quite different in the two types.